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Kinetic investigation of CO_2 reforming of CH_4 over La–Ni based perovskite

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ABSTRACT

The kinetic behavior of the $LaNiO_3$ catalyst in the reforming reaction of methane with carbon dioxide was investigated as a function of temperature and partial pressures of CH_4 and CO_2. There are two kinds of active sites on the catalyst surface. In the first Ni reacts with CH_4 and in the second kind La_2O_3 reacts with CO_2. XRD pattern of the spent catalyst has shown that the phase $La_2O_2CO_3$ has formed which confirmed displayed mechanism. A reaction rate based on the mechanistic results was developed which predicts the experimental reaction rate with a good accuracy. Moreover, the kinetic behavior of $LaNiO_3$ was compared with the Ni/La_2O_3, Rh/La_2O_3 catalysts in the reforming reaction of methane with carbon dioxide at different temperatures and partial pressures of CH_4 and CO_2. These three catalysts have shown the same mechanism and the coefficients of rate equation for each one has been estimated by genetic algorithm. The results showed that Rh/La_2O_3 and $LaNiO_3$ posses more activity than Ni/La_2O_3at higher range of reaction temperature.

1. Introduction

The reforming reaction of methane with carbon dioxide to synthesis gas has received significant attention in the last few years as it constitutes a promising alternative route for the production of synthesis gas [1]. This reaction offer a potential method of reducing the concentrations of CO_2 emitted to the atmosphere [2] also that produce syngas (i.e. $CO + H_2$) with $H_2/CO \leq 1$ ratio, favorable for Fischer Tropsch reactions to produce liquid fuels [3,4].

CO_2 reforming of CH_4 has been carried out on metallic catalysts of group VIII supported by a great variety of oxides. Reported order of activity is as follows: Rh, Ru > Ir > Ni, Pt, Pd > Co > Fe, Cu; however, the catalysts are deactivated by deposition of coke on the surface, although novel metals are less prone to deactivation by this cause, they deactivate with time [5]. An alternative is the use of nickel catalysts, a well-known catalyst for stream reforming [6].

Ni catalysts are of special interest since they present a high initial activity for this reaction, interesting redox properties and relatively low cost. However, it is difficult to prevent sintering of nickel and deposition of carbon at high temperatures [7]. Verykios showed that Ni/La_2O_3 catalyst is more stable than $Ni/\gamma\text{-}Al_2O_3$ and Ni/CaO. In Ni/La_2O_3 catalyst, La_2O_3 phase interacts with CO_2 that this leads to formation $La_2O_2CO_3$ phase [8]. The rate over the Ni/La_2O_3 catalyst increases during the initial 2–5 h of reaction is well correlated with increasing concentration of the $La_2O_2CO_3$ species and format-type species. It seems that the presence of a high concentration of oxidized carbon, presumably $La_2O_2CO_3$ and format-type species on the support in the Ni/La_2O_3 catalyst, plays an important role in enhancing reaction rate [9].

The kinetics of the reaction of CO_2 reforming of methane over the Ni/La_2O_3 catalyst was investigated in the temperature range 650–750 °C. The mechanistic scheme assumes adsorption of CH_4 on Ni, followed by cracking and carbon deposition, as a slow step [10]. CO_2 reacts with La_2O_3 to form $La_2O_2CO_3$ (fast step) [11] and the oxycarbonates react with carbon at the interface of the Ni–$La_2O_2CO_3$ particles (slow step) to produce CO. The inverse water-gas shift reaction occurs simultaneously [9].

To model, simulate, and optimize the reactor, a reliable kinetic equation is needed that is not available in the literature. A few papers have been published in which Rh/La_2O_3, Ni/La_2O_3 and $LaNiO_3$ catalysts have been used for the dry reforming of methane.

The Ni perovskite type oxides ($LaNiO_3$) have received significant attention in the last few years. Because of high dispersion of nickel this catalyst produces very small particles of Ni, in the order of the nanometers. Moreover it has shown good resistance to carbon formation [12]. So, there is an increase in activity and stability [13].After calcinations at 700 °C the only phase that is detected by XRD is $LaNiO_3$ as perovskite structure with a rhombohedral symmetry. After the reduction treatment under hydrogen at 700 °C, whatever the starting material ($LaNiO_3$) the perovskite structure is completely destroyed and the only phases detected by XRD are Ni^0 and La_2O_3. After 1 h time on stream in CO_2/CH_4 reforming only phases Ni^0 and La_2O_3 are observed. This showed that the $LaNiO_3$ catalyst after 1 h of reaction destroyed and Ni^0 and La_2O_3 are formed. After 15 h of CO_2/CH_4 reforming the presence of lanthanum oxo-carbonate $La_2O_2CO_3$ was observed with starting $LaNiO_3$ cata-

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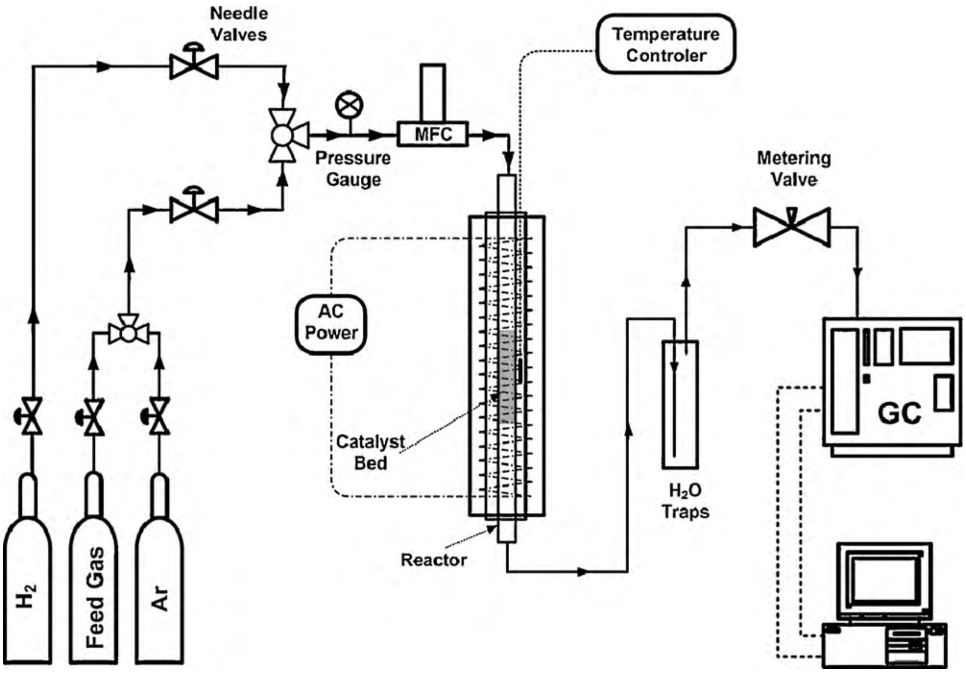

Fig. 1. Schematic view of experimental set up for methane reforming.

lyst [14]. On the basis of the above observations, in the presented mechanism by Verykios for Ni/La_2O_3 catalyst in dry reforming of methane the formation of Ni^0 and La_2O_3 and $La_2O_2CO_3$ phases has been presented.

In this work, Ni perovskite type oxide with the general formula $LaNiO_3$ was synthesized by the sol–gel method and has been used in the reaction of dry reforming of methane at different conditions with varying reactant partial pressures at reaction temperatures ranging from 923 to 1023 K. Then obtained data have been used to evaluate the presented mechanism by Verykios and the required parameters of the rate equation were calculated. Moreover, it was shown that three catalysts including $LaNiO_3$, Ni/La_2O_3 and Rh/La_2O_3 have the same mechanism in dry reforming and kinetic performances were compared.

However $LaNiO_3$ as pervoskite form has different characteristics form Ni/La_2O_3 catalyst but XRD results showed the same species NiO, La_2O_3 and $La_2O_2CO_3$ have been formed at the reaction conditions. Hence the same mechanism has been assumed [9]. Despite of the same form of the reaction rate, reaction rate constants and absorption constants are different.

2. Experimental

2.1. Catalyst preparation

$LaNiO_3$ catalyst was prepared by sol–gel method. In brief, the appropriate amounts of $Ni(NO_3)_2{\cdot}6H_2O$ (Merck, purity 97%) and $La(NO_3)_3{\cdot}6H_2O$ (purity 99%, Merck) dissolved in propionic acid separately and warmed and maintained under reflux condition till about 1 h. Then Ni salt solution was added to La solution under vigorous stirring. The obtained solution was maintained under reflux condition and vigorous stirring for about 4 h till a green gel was formed. The produced gel was dried over night and calcined at 750 °C (ramp 3 °C/min) for 4 h. The obtained catalyst was crushed and used as powder form [15].

2.2. Kinetic measurements

Schematic view of experimental set up has shown in Fig. 1. Kinetic was studied under differential conditions in a conventional flow system consisting of a flow measuring and control system, a mixing chamber, and a fixed-bed quartz reactor (I.D. = 5 mm, H = 60 cm), which was placed in an electric oven. The length of catalyst bed is 2 cm until it avoid gradient temperature in axial length. The reaction carried out under atmospheric pressure at 650, 700 and 750 °C. The feed and product streams were analyzed with a gas chromatograph equipped with a thermal conductivity detector and two pack columns MS and Propack Q for detecting CO, CO_2, CH_4. The mass of catalyst used was 10 mg that diluted with 90 mg silicon carbide (sic, 200–450 mesh) as inert solid. Conversions were usually controlled to be significantly lower than those defined by thermodynamic equilibrium by adjusting the total flow rate (180 ml/min). Rate limitation by external and/or internal mass transfer under differential conditions proved to be negligible by applying suitable experimental criteria.

3. Results and discussion

3.1. Characterization

The specific surface of the prepared $LaNiO_3$ sample is 8 m^2/g which is determined by BET test (Micrometrics flowsorb II 2300 Apparatus). XRD test using X-ray diffractometer with $CuK\alpha = 1.5406$ Å operated at 40 kV and 300 mA for fresh $LaNiO_3$ catalyst showed perovskite structure with a rhombohedral symmetry and XRD of the spent catalyst showed Ni^0, La_2O_3 and $La_2O_2CO_3$. The results are similar to the other researchers [14].

3.2. Mass and heat transport effects

Reliable kinetic data can only be obtained in the absence of mass and heat transport resistances. The effects of interface and intraparticle heat and mass transport resistances on kinetic parameters were determined employing theoretical and experimental procedures. The effect of feed flow rate and catalyst particle size of the $LaNiO_3$ catalyst on reaction rate was determined experimentally with a feed mixture composed of $CH_4/CO_2/He$ (30/30/40 vol.%) at 750 °C.

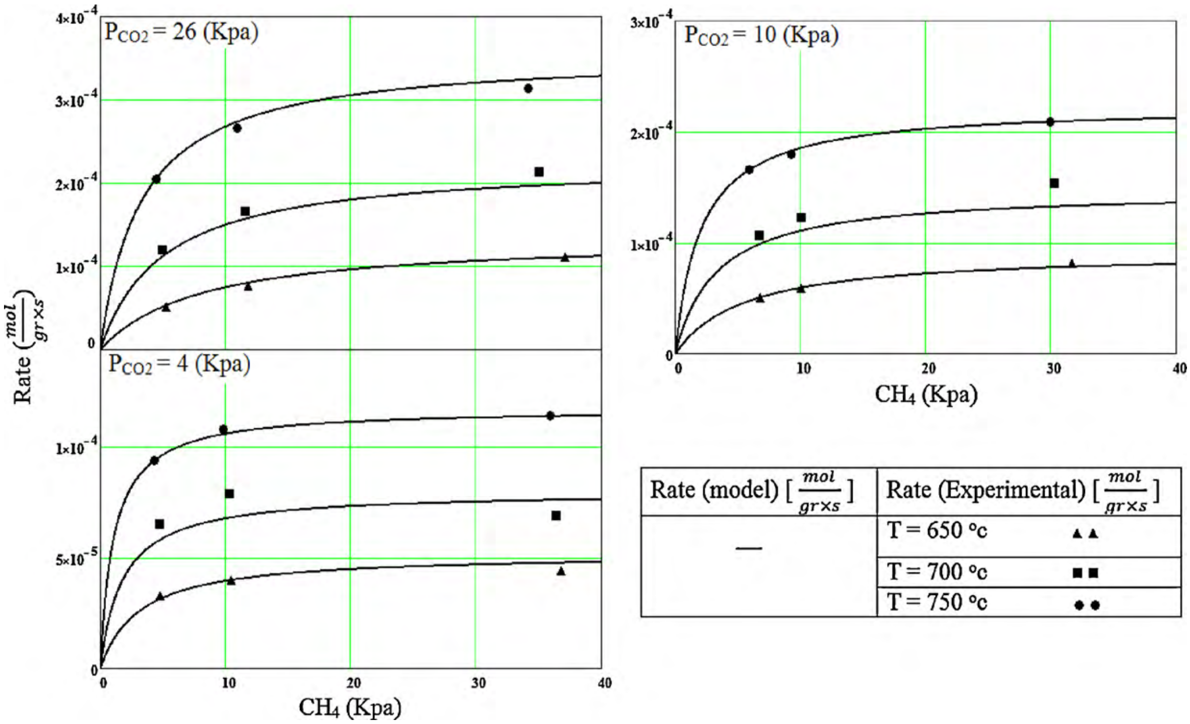

Fig. 2. Rate of methane consumption vs. methane partial pressure at different temperatures and partial pressures of CO_2.

3.3. *Kinetic measurements*

The influence of the partial pressure of reactants on the rate of methane consumption is depicted in Fig. 2. This figure has been drawn in three parts to inhabit from overlapping the plots. These studies were performed at atmospheric pressure in the temperature range of 923–1023 K under differential conditions. The measurements were made maintaining the partial pressure of one reactant constant (4, 10 or 26 kPa) and varying the other reactant pressure in the range of 5–40 kPa. The plots in Fig. 2 have similar shapes, although in terms of the rates obtained at low pressure of either reactant, P_{CH_4} has a stronger influence than P_{CO2} on methane reaction rate (r_{CH_4}). This is symptomatic of a lower reaction order for CO_2 than for CH_4.

3.4. *Proposed mechanism*

There are some studies on the kinetic of the methane reforming reaction with CO_2, over the Rh/La_2O_3 and Ni/La_2O_3 catalysts employing a number of different techniques. So, firstly we tried to use the obtained results based on the observations of previous authors [10,16]. The obtained results are as follows:

Proposed mechanism leads to a reaction rate equation which showed higher rate by increasing methane partial pressure until to some partial pressure of methane around 15 kPa, and then remains nearly constant at higher pressure (Fig. 2). This observation could be concluded that the methane adsorption over active site is at equilibrium.

- After 1 h of time on stream in dry reforming reaction, the starting material nickel perovskite structure ($LaNiO_3$) was completely destroyed and the only phases detected being Ni^0 and La_2O_3 [14].
- A certain fraction of the Ni content of the catalyst is visible by XRD, following the reforming reaction even under integral conditions. This implies that portion of Ni is free of carbon deposits under reaction conditions [17].
- A strong interaction exists between CO_2 and the La_2O_3 support leading to the formation of stable $La_2O_2CO_3$ species, which are detected by FTIR and XRD [18].
- The dry reforming of methane rate at fixed methane concentration shows that the reaction rate increases with the CO_2 concentration up to a CO_2 inlet concentration of about 15 kPa and then reaches asymptotically a plateau (see Fig. 6). Moreover Shirsat et al. showed that the CO_2 adsorption over the La_2O_3 is at equilibrium [19].

The mechanistic picture is that methane reversibly adsorbs on the metallic clusters (Eq. (1)) while the cracking of the adsorbed species proceeds, slowly liberating H_2 and generating carbon that remains on the metallic surface. The CO_2 rapidly reacts with La_2O_3 to generate oxycarbonate, which in turn reacts slowly with carbon (Eq. (4)) to generate the other main product, CO. This slow reaction occurs most likely at the metal/support interface. Note that the RWGS occurs simultaneously all of the time and is always

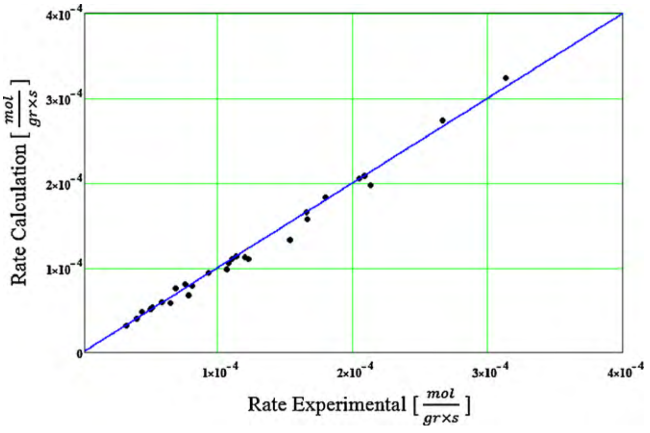

Fig. 3. Parity plots of calculated rate vs. experimental rate.

Table 1
Obtained rate coefficients as a function of temperature.

Catalyst	$K_1\left(\frac{1}{\text{kPa}}\right)$	$k_2\left(\frac{\text{mol}}{\text{g cat s}}\right)$	$K_3k_4\left(\text{kPa}^{-1}\frac{\text{mol}}{\text{g cat s}}\right)$
Rh/La_2O_3	$14\exp\left(\frac{-3030}{T}\right)$	$2.44\exp\left(\frac{-8549}{T}\right)$	$0.12\exp\left(\frac{-4990}{T}\right)$
Ni/La_2O_3	$0.0012\exp\left(\frac{4726}{T}\right)$	$0.24\exp\left(\frac{-6593}{T}\right)$	$3.23E-06\exp\left(\frac{-3525}{T}\right)$
$LaNiO_3$	$297.55\exp\left(\frac{-7502.5}{T}\right)$	$12.27\exp\left(\frac{-10219.2}{T}\right)$	$0.034\exp\left(\frac{-6968.2}{T}\right)$

equilibrated.

$$CH_4 + s \overset{K_1}{\longleftrightarrow} S-CH_4 \quad \text{(equilibrium)} \tag{1}$$

$$S-CH_4 \xrightarrow{k_2} S-C + 2H_2 \quad \text{(slow step)} \tag{2}$$

$$CO_2 + La_2O_3 \overset{K_3}{\longleftrightarrow} La_2O_2CO_3 \quad \text{(equilibrium)} \tag{3}$$

$$La_2O_2CO_3 + S-C \xrightarrow{k_4} La_2O_3 + 2CO + S \quad \text{(slow step)} \tag{4}$$

In the other hand, step (2) could be substituted for a series of elementary H-abstraction steps that can be written as:

$$S-CH_4 \xrightarrow{k_2} S-CH_x + \frac{4-x}{2}H_2 \tag{2a}$$

The rate equation that has been fitted with our data derived assuming that Eqs. (2) and (4) represent the rate-determining steps and that the surface coverage of H_2 and CO adsorbed are negligible.

$$r_{CH_4} = \frac{K_1k_2K_3k_4[CH_4][CO_2]}{K_1K_3k_4[CH_4][CO_2] + K_1k_2[CH_4] + K_3k_4[CO_2]} \tag{5}$$

Note that in the mentioned above mechanism, La_2O_3, Ni^0, $La_2O_2CO_3$ phases have been appeared. In the $LaNiO_3$ catalyst after reaction also these phases have been seemed [14]. Based on these

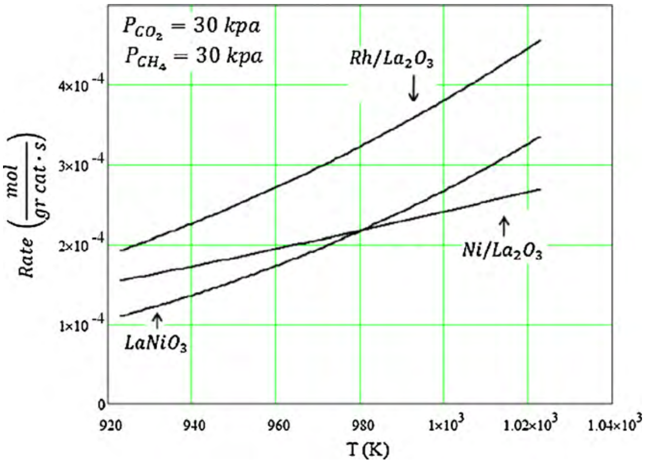

Fig. 4. Rate of methane consumption for Ni/La_2O_3, Rh/La_2O_3 and $LaNiO_3$ catalysts in dry reforming of methane.

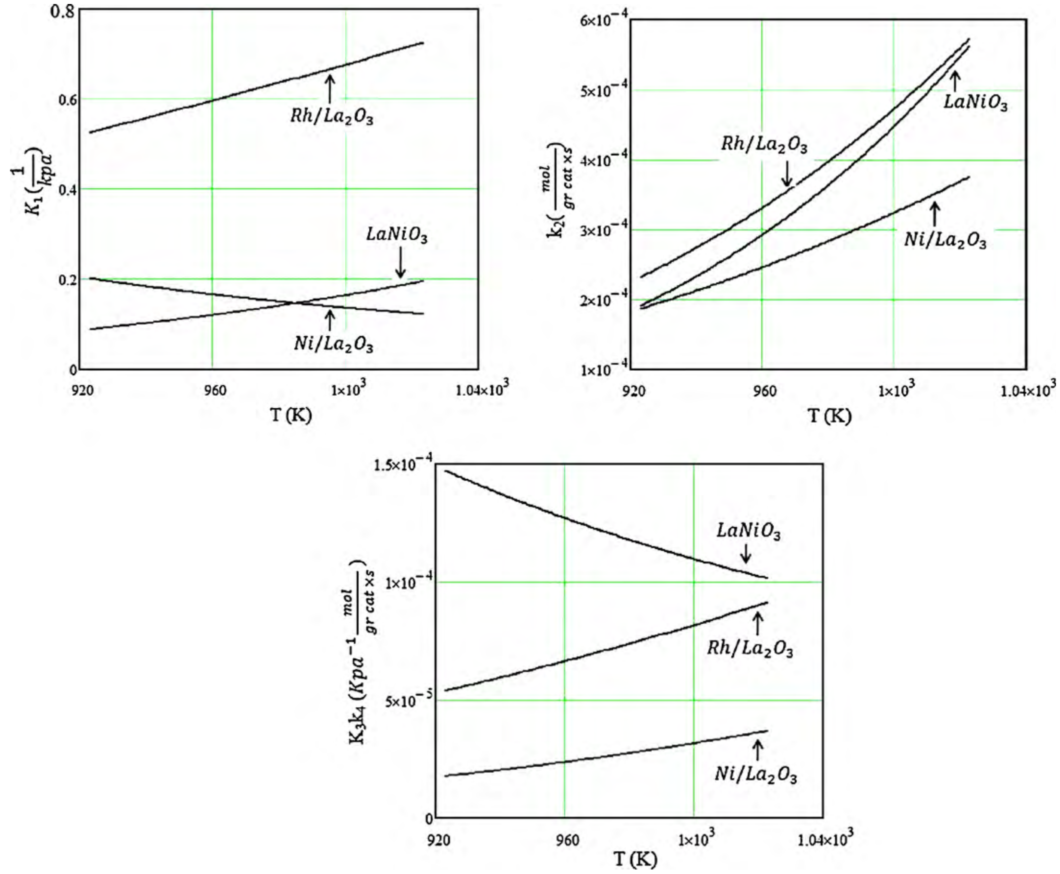

Fig. 5. Comparison of the kinetic coefficients of the Ni/La_2O_3, Rh/La_2O_3 and $LaNiO_3$ catalysts in dry reforming of methane for different temperatures.

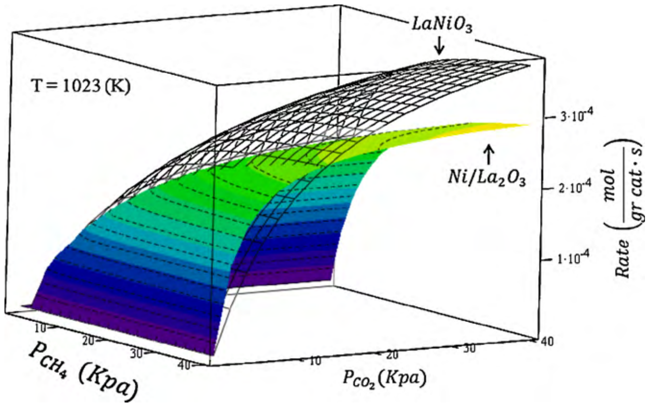

Fig. 6. Rate of reaction vs. partial pressure of reaction species CO_2 and CH_4.

phases, it has been assumed that the presented mechanism for $LaNiO_3$ catalyst is accessible.

Using Eq. (5), our data were fitted properly, as shown in Fig. 3 ($R^2 = 0.98$). Rate equation coefficients (K_1, k_2 and k_3k_4) has obtained for $LaNiO_3$ by genetic algorithm and for Ni/La_2O_3 catalyst was given by Verykios [10] and for Rh/La_2O_3 was given by Cornaglia [16]. The result showed in Table 1. Where K_1 is the equilibrium constant of methane adsorption and k_2 is the rate constant of the decomposition (cracking) of methane on the Ni surface. K_3 is the equilibrium constant of reaction (3), and k_4 represents the kinetic constant of reaction (4). These two constants K_3 and k_4 could not be determined individually from experimental data. But a value for K_3 has reported by Shirsat et al. as follow [19]:

$$K_3 = 5.817 \times 10^{-9} \exp\left(\frac{17502.2}{T}\right)\left(\frac{1}{\text{kPa}}\right) \tag{6}$$

As illustrated in Fig. 4, Rh/La_2O_3 catalyst activity is more than Ni/La_2O_3 and $LaNiO_3$ catalysts at dry reforming reaction. Higher activity could be attributed to higher values of K_1 and k_2 coefficients at the operating temperature range. So, Rh/La_2O_3 catalyst adsorbs higher amount of methane (higher K_1) and posses higher decomposition reaction rate constant for methane (k_2) on the active sites which resulted higher activity. Coefficients of the rate equation for three catalysts (Rh/La_2O_3, Ni/La_2O_3 and $LaNiO_3$) have been drawn in Fig. 5 for comparison.

Also, CH_4 consumption rate was plotted in Fig. 6 as a function of CO_2 and CH_4 partial pressures at constant temperature (1023 K). As shown at the low pressure of CO_2 and CH_4, the activity of $LaNiO_3$ catalyst is lower than Ni/La_2O_3 catalyst. But at the high range of pressure the activity of $LaNiO_3$ catalyst is higher than Ni/La_2O_3 catalyst.

4. Conclusion

Investigation the mechanism and rate equation of CO_2 reforming of methane on $LaNiO_3$ catalyst showed that perovskite structure destroyed and La_2O_3 and Ni^0 formed at the conditions of reaction (T ≥ 700 °C) then CO_2 with La_2O_3 produce $La_2O_2CO_3$ phase which in turn reacts with the carbon that was adsorbed on Ni^0 site and produce CO. Hydrogen is produced from decomposition of adsorbed methane directly. This behavior is similar to the Ni/La_2O_3catalyst in dry reforming with some difference in temperature dependency terms including adsorption equilibrium constants (K_1, K_3) and reaction rate constants (k_2, k_4).

$LaNiO_3$, Ni/La_2O_3, Rh/La_2O_3 kinetic performances were investigated. All catalysts showed same mechanism, so a single kinetic relation could be used however for each catalyst corresponding kinetic data should be used for coefficients estimation. With comparing coefficients of the rate equation for each catalyst, effect of any stages of mechanism on the rate can be identified. For example the activity of Rh/La_2O_3 is more than Ni/La_2O_3 and $LaNiO_3$ which could be attributed to higher values of CH_4 adsorption and methane decomposition rate in the mechanism (Eqs. (1) and (2)). Also, it was concluded that the activity of Ni/La_2O_3 and $LaNiO_3$ catalysts were affected by temperature and pressure. In low range of concentration, the activity of Ni/La_2O_3 is more than $LaNiO_3$. So it is recommended to use $LaNiO_3$ catalyst in the feed entering section of the catalyst bed where reactants concentration is higher and Ni/La_2O_3 in the outlet section of catalyst bed of reactor that has a lower reactants concentration.

References

[1] J.R.H. Ross, A.N.J. van Keulen, M.E.S. Hegarty, K. Seshan, Catal. Today 30 (1996) 193.
[2] K. Tomishige, Y.G. Chen, K. Fujimoto, J. Catal. 181 (1999) 91.
[3] L. Bedel, A.-C. Roger, J.-L. Rehspringer, Y. Zimmermann, A. Kiennemann, J. Catal. 235 (2005) 279.
[4] M.E. Dry, Catal. Today 71 (2002) 227.
[5] M.C.J. Bradford, M.A. Vannice, Catal. Rev. 41 (1999) 1.
[6] H.S. Bengaard, J. Catal. 209 (2002) 365.
[7] T. Horiuchi, K. Sakuma, T. Fukui, Y. Kubo, T. Osaki, T. Mori, Appl. Catal. 144 (1996) 111.
[8] Z. Zhang, X.E. Verykios, Appl. Catal. 138 (1996) 109.
[9] V.A. Tsipouriari, X.E. Verykios, Catal. Today 64 (2001) 83.
[10] X.E. Verykios, Int. J. Hydrogen Energy 28 (2003) 1045.
[11] A. Slagtern, Y. Schuurman, C. Leclerc, X. Verykios, C. Mirodatosy, J. Catal. 172 (1997) 118.
[12] T. Borowiecky, Appl. Catal. 10 (1984) 273.
[13] M.R. Goldwasser, M.E. Rivas, E. Pietri, M.J. Perez-Zurita, M.L. Cubeiro, L. Gingembre, L. Leclercq, G. Leclercq, Appl. Catal. 255 (2003) 45.
[14] G.S. Gallego, F. Mondragon, J. Barrault, J.-M. Tatibouet, C. Batiot-Dupeyrat, Appl. Catal. 311 (2006) 164.
[15] G. Valderrama, A. Kiennemann, M.R. Goldwasser, Catal. Today 133–135 (2008) 142.
[16] J.F. Munera, S. Irusta, L.M. Cornaglia, E.L. Lombardo, D.V. Cesar, M. Schmal, J. Catal. 245 (2007) 25.
[17] C. Batiot-Dupeyrat, G. Valderrama, A. Meneses, F. Martinez, J. Barrault, J.M. Tatibouet, Appl. Catal. 248 (2003) 143.
[18] V.A. Tsipouriari, X.E. Verykios, J. Catal. 187 (1999) 85.
[19] A.N. Shirsat, M. Ali, K.N.G. Kaimal, S.R. Bharadwaj, D. Das, Thermochim. Acta 399 (2003) 167.